TORA

Derivatives

OF

New Complex Inorganic Acids.

THESIS

Presented to the Faculty of the Department of Philosophy of the University
of Pennsylvania in Partial Fulfilment of the Requirements for the
Degree of Doctor of Philosophy

BY

ALLEN ROGERS, M. S.
UNIVERSITY OF MAINE.

PHILADELPHIA:
INTERNATIONAL PRINTING CO.
1902

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Introduction.

The object in mind when this investigation was undertaken, was to see if a compound could be prepared, by synthesis, corresponding to the black crystals obtained by Smith and Exner (*Jour. Am. Chem. Soc.*, **24**,573), from the mother liquor of ammonium tungstate.

These black crystals on examination were found to contain tungsten, vanadium, phosphorus and ammonia, together with traces of manganese and iron. A careful study revealed the fact that the body in hand had a definite composition, and that it was a salt of some new complex inorganic acid. In order to determine its true constitution a quantitative analysis was undertaken, in which the methods as proposed by Gibbs (*Am. Ch. J.*, **1**, 1, 217; **2**, 3119; **4**, 377; **5**, 391; **7**, 313, 392), Friedheim (**B, 1890**, 353, 1503, 1530, 2600), Kehrmann (**B. 20,** 1805, 1811; **24,** 2326; **A. 245,** 45; *Z für anorg. Ch.* **I**, 428), and Fremery (**B. 1884,** 296), were employed. The results were not satisfactory, and it was evident that a good analytical method was one of the first problems to be solved.

In the development of this method of analysis it was essential that the substance under examination should have a fair degree of purity. To accomplish this, it was necessary to start with pure chemicals, and from them to prepare a compound similar to the one in question. To arrive at this result, a mixture of ammonium tungstate, ammonium vanadate, and ammonium phosphate were boiled together for several hours. On evaporating the solution, red crystals were obtained in place of the black ones which had been anticipated. These, too, on examination, were found to contain tungsten, vanadium, phosphorus, and ammonia. A new difficulty was thus presented; but one which was quickly solved, and together with other observations will be set forth in the following pages.

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Experimental Part.

AMMONIUM PHOSPHO-VANADO-TUNGSTATE.

$13\,(NH_4)_2O.\ 2P_2O_5.\ 8V_2O_5.\ 34WO_3 + 86H_2O.$

Preparation.—In the preparation of this salt various amounts of ammonium phosphate, ammonium vanadate, and ammonium tungstate were boiled together for six hours. The solution after filtration was evaporated and allowed to crystallize. The crystals formed in every case were identical in physical appearance and, as will be seen later, had the same chemical composition.

The best results were obtained when 1 grm. of ammonium phosphate, 15 grms. of ammonium tungstate, 3 grms. of ammonium vanadate, 20 c.c. of ammonium hydrate, and 700 c.c. of water were brought together, in a liter flask, and boiled for six hours. At first the solution was colorless, but soon changed to yellow and then to red. At this point the ammonium tungstate dissolved very rapidly, and the solution became much darker in color. The slight residue was filtered off, and the filtrate evaporated to a sp. gr. of 1.115. On standing over night the salt separated. The mother liquor was again evaporated, and a second crop of crystals was obtained.

Properties.—The product of the above procedure gave dark red crystals, which were octahedra and cubes in form; very soluble in cold and hot water; insoluble in alcohol, ether, carbon disulphide, benzene, and nitrobenzene. No change was produced when the crystals, reduced to a fine powder, were treated with dilute nitric or hydrochloric acid. Strong hydrochloric acid gave a yellow precipitate, with the evolution of chlorine on boiling. Strong nitric acid produced a yellow precipitate, which dissolved on the addition of water.

With ammonium hydrate there was no change. Caustic potash or soda gave a yellow precipitate, which dissolved on boiling, with the evolution of ammonia. Mercurous nitrate formed a yellow precipitate, which turned red when dry; insoluble in boiling water or excess of reagent; but rendered soluble by a few drops of nitric acid. This precipitate was found to be the mercury salt of phospho-vanado-tungstic acid, and from it the acid was prepared. A discussion of this acid, and its salts with the heavy metals, is not within the scope of this paper. It may not, however, be out of place to give some of the principal points at this time. Starting with ammonium phospho-vanado-tungstate, the silver or mercury (better silver) salt was precipitated. This precipitate was washed, and dried; or in most cases was placed in a flask with a few drops of nitric acid and brought to boiling. When the solution was complete it was filtered and evaporated to a low bulk, and on standing over night black needle-shaped crystals of silver phospho-vanado-tungstate were deposited. These crystals were removed and dissolved in water, and to the solution hydrochloric acid was added, a few drops at a time, until all of the silver was precipitated. The silver chloride was filtered off and the filtrate evaporated on the water bath to a small volume. From this solution the acid was deposited in dark red octahedral crystals. A solution of this acid gave the same reactions with the heavy metals as those produced by the ammonium salt. With ammonium phospho-vanado-tungstate, and also with phospho-vanado-tungstic acid the precipitates formed were found to be due to the deposition of metallic derivatives of the above-mentioned acid.

To come back to the ammonium salt again: It was found that copper nitrate produced no change in the solution; but when ammoniacal copper nitrate was added a red precipitate was formed, insoluble in boiling water, but dissolved very readily when a few drops of nitric acid were added. Ammoniacal cadmium chloride gave an orange colored precipitate, slightly soluble in boiling water; rendered soluble by nitric acid. Stannous chloride gave a gray precipitate, rapidly taking on a blue tint. Ammoniacal cobalt nitrate produced a greenish gray precipitate, which turned red when dried. Zinc acetate gave a yellow precipitate, quite soluble in boiling water. Barium chloride in an ammoniacal solution gave a light yellow precipitate, which remained insoluble on boiling; but dissolved readily when a little nitric acid was added.

Method of Analysis.—As stated above the method proposed by Gibbs and Friedheim could not be used in the analysis of the black crystals from wolframite; neither were they applicable to this salt. After trying various means the following was found to give very satisfactory results:

The air dried salt was reduced to a fine powder, and a known quantity introduced into a tared crucible. It was heated gently at first, then the temperature was increased, and continued until constant weight was obtained. The loss represented the water and ammonium oxide. The residue was boiled with dilute nitric acid in which the vanadium pentoxide and phosphorus pentoxide dissolved, leaving the tungsten trioxide insoluble. After standing several hours the precipitate was filtered off. It was washed with a little water containing nitric acid, dried, ignited, and weighed as tungsten trioxide. The tungsten trioxide nearly always held some vanadium pentoxide which was removed by gently heating in a current of hydrochloric acid gas. The filtrate from the tungsten trioxide was evaporated to dryness in a weighed porcelain crucible on the water bath, and then gently heated over the flame. The mass fused. In this way the combined weight of the phosphorus pentoxide and vanadium pentoxide was determined. The fusion was taken up with water containing a little nitric acid, in which it dissolved readily on warming. The phosphorus pentoxide was thrown out with a magnesia mixture. The ammonium magnesium phosphate was dissolved in dilute nitric acid, and reprecipitated by addition of ammonium hydrate, when it came down free from vanadium. The vanadium pentoxide was then determined by difference. To make sure, however, that the difference was vanadium pentoxide, in a number of cases, vanadium was thrown out from the filtrate, with concentrated ammonium chloride and alcohol. On ignition of the ammonium vanadate so found vanadium pentoxide was produced, which in each case corresponded to the amount obtained by difference. The ammonium oxide was ascertained by boiling a new portion of the salt with caustic potash. The liberated ammonia being collected in a standard solution of hydrochloric acid, and the excess titrated with ammonium hydrate. The ammonium oxide found by this means was subtracted from the ammonium oxide and water determined by ignition. The difference gave the true water content.

Result of Analysis.—The percentages as given below are for salts prepared from eight different combinations. It shows, therefore, that the same compound was always produced.

	Theory.	Found.	Found.	Found.	Found.	Found.	Found.	Found.	Found.
$(NH_4)_2O$	5.71	5.72	5.77	5.77	5.57	5.87	5.59	5.59	5.89
P_2O_5	2.39	2.32	2.60	2.60	2.43	2.52	2.33	2.51	2.25
V_2O_5	12.28	12.09	12.25	11.91	12.50	12.23	12.03	11.68	12.07
WO_3	66.55	66.33	66.39	66.32	66.35	66.44	66.41	66.39	66.35
H_2O	13.07	13.17	12.78	13.16	13.09	12.97	13.63	13.77	12.84
	100.00	99.63	99.89	99.76	99.94	100.03	99.99	99.94	99.40

As has been observed, a red salt was formed in each case. It was evident, then, that the black color, of the product from the mineral, was due to some other factor than to the combining ratio. It was later discovered that this black color was caused by the reduction of vanadium to a lower oxide. With this idea in view the following salt was prepared :

AMMONIUM PHOSPHO-VANADICO-TUNGSTATE.

$15\,(NH_4)_2O.\ 2\,P_2O_5.\ 6V_2O_3.\ 44WO_3 + 106\ H_2O.$

Preparation.—The salt was obtained by bringing together 1 grm. of ammonium phosphate, 15 grms. of ammonium tungstate, 1.1 grms. of vanadium trioxide (prepared by treating 1.6 grm. of ammonium vanadate with strong hydrochloric acid, and evaporating to dryness on a water bath), 25c.c. of ammonium hydrate with 700c.c. of water, and boiling the mixture for six hours. By this means a black solution resulted, which was evaporated to a sp. gr. of 1.030 and allowed to stand over night in a cool place. The crystals obtained had a deposit of ammonium chloride on the surface. This was removed by washing them with a little cold water and the product was finally dried on filter paper.

Properties.—The salt as prepared in the above manner gave black crystals with octahedral and cubic habit, the octahedral being far in excess and truncated by four of the cubes. The compound was soluble in water; insoluble in alchohol, ether or benzene. Dilute nitric acid produced a slight change in color on boiling. The same thing being true of dilute hydrochloric acid. Strong hydrochloric acid produced a yellow precipitate, but without the evolution of chlorine on boiling. Concentrated nitric acid gave a yellow precipitate, which dissolved on adding water. Ammonium hydrate produced no change. Potassium hydrate gave a yellow precipitate, which partly dissolved on boiling, at the same time giving off ammonia, while a black residue remained. Mercurous nitrate gave a yellow precipitate, which remained insoluble on boiling, but dissolved on adding a little nitric acid. Silver nitrate gave a greenish black precipitate. Barium chloride produced a gray precipitate which dissolved when heated, but separated again on cooling. The composition of the salt was very much like that obtained from the mother liquor of ammonium paratungstate, but differed from it in some of its properties.

Method of Analysis.—The same method was applied as for the first salt, except that the resulting vanadium pentoxide was calculated into vanadium trioxide, and the difference added to the percentage of water of crystallization.

Result of Analysis:—

	Theory.	Found.	Found.	Found.	Found.	Found.
$(NH_4)_2O$	5.53	5.44	5.44	5.32	5.32	5.35
P_2O_5	2.02	1.94	2.03	1.84	1.94	1.94
V_2O_3	6.39	6.34	6.34	6.32	6.06	6.26
WO_3	72.50	72.34	72.23	72.55	72.99	72.52
H_2O	13.56	13.60	13.59	13.43	13.69	13.55
	100.00	99.66	99.63	99.46	100.00	99.62

AMMONIUM PHOSPHORICO-VANADO-TUNGSTATE.

It was thought that this salt would result when ammonium phosphite, ammonium tungstate and ammonium vanadate were brought together. Such, however, was not the case. The compound produced being ammonium phospho-vanadico-tungstate. This, no doubt, was due to the reducing action of phosphorus trioxide on vanadium pentoxide.

AMMONIUM PHOSPHORICO-VANADICO-TUNGSTATE.

$14(NH_4)_2O. 2P_2O_3. 7V_2O_3. 31WO_3 + 78H_2O.$

Preparation.—The next thought to present itself for consideration was to see if a salt could be prepared having the phosphorus and vanadium both in the lower state of oxidation. To accomplish this, 1.5 grms. of ammonium phosphite, 1 grm. of vanadium trioxide, 20 grms. of ammonium tungstate, 25 c.c. of ammonium hydrate, and 700 c.c. of water were brought together. After boiling for five hours, the black solution was filtered, and evaporated to about one-fourth of its original volume.

Properties.—The resulting black octahedral crystals were soluble in water; insoluble in alcohol, ether, carbon disulphide, and benzene. The action of dilute or strong nitric or hydrochloric acid, mercurous nitrate, or even silver nitrate was the same as in the previous salt. Barium chloride produced no change when first added to the solution; on standing, an olive-green precipitate was formed.

Method of Analysis.—The same method was used as in former cases; except that a few drops of nitric acid were added to the mass after ignition. The excess of acid was driven off by warming in the water bath, and the crucible again strongly heated. The resulting vanadium pentoxide and phosphorus pentoxide were calculated to vanadium trioxide and phosphorus trioxide, the difference being added to the percentage of water.

These seem to be all of the possible combinations in this series; that is, in which we have one base united to one oxide of each of the three acid forming elements.

Result of Analysis:—

	Theory.	Found.	Found.	Found.	Found.	Found.
$(NH_4)_2O$	6.85	6.80	6.86	6.86	6.75	6.75
P_2O_3	2.07	2.03	2.02	1.94	2.11	2.00
V_2O_3	9.89	10.08	10.21	10.06	9.91	9.38
WO_3	67.98	67.91	67.73	66.77	68.11	68.02
H_2O	13.21	12.93	12.45	12.77	12.74	13.74
	100.00	99.75	99.54	99.40	99.62	99.89

It has been demonstrated that phosphorus, vanadium, and tungsten combine to form a series of complex inorganic acids. These acids have also been shown to be stable bodies, and capable of giving salts with many basic radicals. The reactions obtained with the heavy metals show a difference from those produced by salts of any of the individual members. The conclusion drawn from these reactions and the constant composition given by analysis is that the compounds under consideration are definite bodies, and not mixtures of phosphates, vanadates, and tungstates.

In the same group with phosphorus is arsenic. This element has many properties in common with phosphorus. The question arose: Can we have a series of compounds in which arsenic takes the place of the phosphorus? The idea appeared to be plausible. Ammonium arsenate and ammonium arsenite were, therefore, substituted for the corresponding phosphorus salt and the following series of compounds prepared:

Ammonium arseno-vanado-tungstate.
Ammonium arseno-vanadico-tungstate, and
Ammonium arsenico-vanadico-tungstate.

AMMONIUM ARSENO-VANADO-TUNGSTATE.

$$18(NH_4)_2O.\ 2As_2O_5.\ 13V_2O_5.\ 39WO_3+88H_2O.$$

Preparation.—To 700 c.c. of water, made alkaline with 15 c.c. of ammonium hydrate, 1 grm. of ammonium arsenate, 15 grms. of ammonium tungstate and 1 grm. of ammonium vanadate were added. The mixture was heated to boiling and maintained at that temperature for five hours. The solution was, at first, colorless; but soon changed to yellow, and then to red, but not so dark red as in the case of the phospho-salt. The filtered solution was evaporated and on standing over night the salt separated.

Properties.—The small octahedral crystals which were formed above were soluble in water, but insoluble in organic solvents. Dilute hydrochloric acid or nitric acid was without action. When boiled with strong hydrochloric acid chlorine was evolved, and a yellow precipitate produced ; on further boiling the precipitate dissolved, but reappeared when the solution had become cold, or on the addition of water. Mercurous nitrate gave a yellow precipitate, which remained insoluble on boiling, but dissolved when nitric acid was added. From this precipitate it seems probable that the acid can be obtained. Silver nitrate gave a red precipitate, soluble in boiling water, hastened by a drop or two of nitric acid. Lead acetate, ammonical copper nitrate or other salts of the heavy metals gave precipitates, which resembled those obtained from the corresponding phospho-compound. As far as studied, these precipitates were derivatives of arseno-vanado-tungstic acid. A more complete study, however, may bring out many interesting facts. But as the purpose of this paper is to point to the different possibilities, rather than to go too much into detail, we will leave the thought, and, as time goes on, and more work is carried out in this line of investigation, let us hope that the gaps may be filled, and that the completed structure may have its proper place in the great family of inorganic compounds.

Method of Analysis.—The same procedure was employed as for the phospho-salts.

Result of Analysis :—

	Theory.	Found.	Found.	Found.	Found.	Found.
$(NH_4)_2O$	6.51	6.63	6.63	6.73	6.73	6.68
As_2O_5	3.18	3.17	2.94	3.11	3.11	3.08
V_2O_5	16.39	16.80	16.75	16.22	16.26	16.51
WO_3	62.95	62.70	62.75	62.81	62.86	62.80
H_2O	10.97	10.54	10.51	10.83	10.58	10.61
	100.00	99.84	99.58	99.70	99.54	99.68

AMMONIUM ARSENO-VANADICO-TUNGSTATE.

$17 (NH_4)_2O. 2 As_2O_5. 14\frac{1}{2}V_2O_3. 29WO_3+98H_2O.$

Preparation.—In the synthesis of this body 1 grm. of ammonium arsenate, 15 grms. of ammonium tungstate, 1 grm. of vanadium trioxide, 25 c.c. of ammonium hydrate and 700 c.c. of water were boiled for five hours. The filtered solution was evaporated on the water bath to about one-half of the original volume. It was then removed to a cool place and allowed to stand over night. The crystals were usually covered with a deposit of ammonium chloride which was removed by a little cold water. The crystals from the mother liquor were often mixed with other salts. In order, therefore, to get concordant results, the first crop of crystals were the ones submitted to analysis.

Properties.—The salt, as prepared above, gave black octahedral crystals, sparingly soluble in cold water; readily soluble in boiling water; insoluble in alcohol, ether, benzene, carbon disulphide, chloroform, acetone, acetic anhydride, nitrobenzene, and aniline. Dilute nitric acid produced a change in color from black to red. Dilute hydrochloric acid changed the color likewise when it was boiled with this reagent. Strong nitric acid gave a yellow precipitate, which dissolved on addition of water. Strong hydrochloric acid gave a yellow precipitate. Mercurous nitrate produced a red precipitate, which remained insoluble on boiling, but dissolved when nitric acid was added. Silver nitrate gave a dark green precipitate. An attempt was made to get the acid from this salt, but through the action of nitric acid an oxidation took place, the result being that arseno-vanado-tungstic acid was produced. It may be possible, however, to liberate arseno-vanadico-tungstic acid by some other method, and from the acid so obtained many new compounds would result.

Method of Analysis.—The same method as used for the corresponding phospho-salt was used in this case.

Result of Analysis :—

	Theory.	Found.	Found.	Found.	Found.
$(NH_4)_2O$	7.34	7.26	7.25	7.29	7.29
As_2O_5	3.82	3.77	3.80	3.77	3.62
V_2O_3	18.06	18.11	18.06	17.33	18.17
WO_3	56.12	56.04	55.99	56.04	56.07
H_2O	14.66	14.41	14.46	14.35	14.40
	100.00	99.59	99.56	99.78	99.55

AMMONIUM ARSENICO-VANADO-TUNGSTATE.

By analogy, the production of this compound was looked upon as improbable. A mixture, however, of ammonium arsenite, ammonium vanadate and ammonium tungstate was boiled for six hours. The solution turned dark in color, and finally became black, due to the formation of ammonium arseno-vanadico-tungstate. It may be possible, however, under proper conditions to obtain this salt, as the reduction is not so marked as in the case of the ammonium phosphorico-vanado-tungstate.

AMMONIUM ARSENICO-VANADICO-TUNGSTATE.

$16 (NH_4)_2O. 5 As_2O_3. 15 V_2O_3. 26 WO_3 + 101 H_2O.$

Preparation.—In the production of this compound the same line of thought suggested itself as in case of the corresponding phosphorico-salt. If vanadium could unite with arsenic as arsenic pentoxide in two ways, it seemed probable that it would unite with it as arsenic trioxide. A number of different combinations were tried to determine this, but on boiling together 1 grm. of arsenic trioxide, 12 grms. of ammonium tungstate, 1 grm. of vanadium trioxide, 50 c.c. of ammonia and 700 c.c. of water the best results were obtained. After boiling for five hours the solution was evaporated to about one-half its original volume. On standing in a cool place for twenty-four hours the salt separated.

Properties.—Black octahedral crystals sparingly soluble in cold water, which dissolved readily when boiled. Dilute nitric acid produced a change in color. Strong hydrochloric acid gave a yellow precipitate. Nitric acid gave a yellow precipitate, which remained insoluble on boiling, but dissolved when water was added. Silver nitrate produced a greenish black precipitate, which readily dissolved on the addition of a little nitric acid. Barium chloride gave a gray precipitate, insoluble on boiling; readily soluble in dilute nitric acid.

Result of Analysis:—

	Theory.	Found.	Found.	Found.
$(NH_4)_2O$	6.96	7.02	7.02	7.02
As_2O_3	8.28	8.26	8.12	8.41
V_2O_3	18.83	18.97	18.95	18.99
WO_3	50.70	50.69	50.57	50.71
H_2O	15.23	15.18	15.23	15.13
	100.00	100.12	99.89	100.26

AMMONIUM PHOSPHO-VANADO-VANADICO-TUNGSTATE.

$$29(NH_4)_2O.\ 4P_2O_5.\ 7V_2O_5.\ 13V_2O_3.\ 54WO_3 + 146H_2O.$$

Preparation.—After proving that compounds could exist in which the phosphorus and vanadium were in either stage of oxidation, the question arose: Can a compound be prepared in which the same element is present in both conditions? It seemed possible as Gibbs has shown that such bodies can exist. It remained to determine if the presence of phosphorus would have any affect on the combination. For the preparation of this salt, 1 gram of ammonium phosphate, 1 gram of ammonium vanadate, 1 gram of vanadium trioxide, 16 grams of ammonium tungstate, 30 c.c. of ammonium hydrate, and 700 c.c. of water were used. The boiling of this mixture was continued for five hours. The solution was then filtered, and the greenish black liquid was evaporated on the water bath, when reduced to about one-half of the original volume it was set aside to crystallize.

Properties.—The product obtained from the above solution gave greenish black octahedral crystals, which were sparingly soluble in cold water, but dissolved on boiling. Dilute nitric acid or hydrochloric acid changed the color to red. Strong hydrochloric acid decomposed it, with evolution of chlorine. Strong nitric acid gave off fumes of nitrogen peroxide, while a green precipitate was produced, which dissolved on addition of water. Mercurous nitrate gave a yellow precipitate, which remained insoluble on boiling; but dissolved when nitric acid was added. Barium chloride produced a greenish gray precipitate, which dissolved on boiling, but reappeared when cooled.

Method of Analysis.—The procedure was, for the most part, the same as in former cases. The total vanadium was determined as vanadium pentoxide. A separate portion was boiled with hydrochloric acid, when vanadium pentoxide was reduced to vanadium trioxide, with the elimination of chlorine. The evolved gas was conducted into a solution of potassium iodide, and the liberated iodine titrated with standard sodium thiosulphate.

$I_4 : V_2O_5 :: \text{Amt of } Na_2S_2O_3 \times \text{Strength} : x.$

The true amount of vanadium pentoxide was thus ascertained. This result subtracted from the total vanadium gave the vanadium pentoxide from which the vanadium trioxide was calculated.

Result of Analysis :—

	Theory.	Found.	Found.	Found.
$(NH_4)_2O$	7.35	7.34	7.23	7.23
P_2O_5	2.77	2.66	2.74	2.57
V_2O_5	6.22	6.31	6.34	6.34
V_2O_3	9.51	9.54	9.59	9.48
WO_3	61.34	61.28	61.40	61.15
H_2O	12.81	12.74	12.66	12.83
	100.00	99.87	99.96	99.60

AMMONIUM ARSENO-VANADO-VANADICO-TUNGSTATE.

$35(NH_4)_2O.\ 4As_2O_5.\ 7V_2O_5.\ 16V_2O_3.\ 66WO_3. + 163H_2O.$

Preparation :—From the readiness with which arsenic entered into combination in the salts already studied, it seemed likely that a body related to the one just given could be prepared by introducing arsenic pentoxide in place of phosphorus pentoxide. This was accomplished by using 1 gram of ammonium arsenate, 1 gram of ammonium vanadate, 1 gram of vanadium trioxide, 16 grams of ammonium tungstate, 30 c.c. of ammonium hydrate, and 700 c.c. of water.

The boiling was continued for four hours. The solution, which was greenish black in color, was evaporated on the water bath until it had reached about one-half its original volume. It was then filtered while hot; and being placed in a crystallization dish, was set aside to cool. In most cases at the end of twenty-four hours the salt had separated. The mother liquor was again evaporated and a second crop of crystals was obtained. The yield of salt was much larger in these vanado-vanadico-compounds than in the vanadico-salt.

Properties.—The body produced in this case gave crystals which were black in color, and belonged to the same class as in former cases. The deposit of ammonium chloride was removed by washing with cold water. The solubility was the same as usual. Dilute nitric or hydrochloric acid changed the color of the solution from black to light red. Strong hydrochloric acid decomposed the salt giving off chlorine, and producing a bright yellow precipitate of the hydrated oxide. Nitric acid gave an orange colored precipitate, soluble on the addition of water. Mercurous nitrate, and barium chloride gave olive green precipitates insoluble in boiling water, but soluble on addition of a few drops of nitric acid.

Analysis.—The method employed for this salt was the same as in the previous case.

Result of Analysis:—

	Theory.	Found.	Found.	Found.
$(NH_4)_2O$	7.38	7.42	7.42	7.42
As_2O_5	3.72	3.71	3.79	3.63
V_2O_5	5.15	5.18	5.13	5.13
V_2O_3	9.70	9.54	9.56	9.51
WO_3	62.19	62.12	62.04	62.20
H_2O	11.86	11.84	11.84	11.84
	100.00	99.81	99.78	99.73

It was impossible to introduce phosphorus or arsenic in two conditions, at the same time having vanadium present as vanadium pentoxide. The reason for this being that a reduction of the vanadium pentoxide took place. At the same time the phosphorus or arsenic was oxidized to the higher condition. Were it not for the strong reducing action of arsenic trioxide and phosphorus trioxide we could expect to obtain six new salts in the above manner. As a matter of fact, it was only possible to get two.

AMMONIUM PHOSPHO-ARSENO-VANADO-TUNGSTATE.

$82(NH_4)_2O.\ 12P_2O_5.3As_2O_5.\ 52V_2O_5.\ 201WO_3+567H_2O.$

Preparation.—After having obtained salts, in which the vanadium was present in two stages of oxidation, the question arose: Is it possible to have phosphorus and arsenic together with the vanadium? The thing to ascertain was if the arsenic and phosphorus would unite, or if the phosphorus would produce one body, and the arsenic another. This could only be determined by analysis of the first and second crop of crystals.

In the preparation of the salt, 1 grm. of ammonium phosphate, 1 grm. of ammonium arsenate, 2 grms. of ammonium vanadate, 16 grms. of ammonium tungstate, 20 c.c. of ammonium hydrate, and 700 c.c. of water were boiled for six hours. The solution, which had taken on a deep red color, was filtered while hot. It was then evaporated to one-fourth its original volume, and on standing over night, the salt was deposited. A second crop of crystals was obtained from the mother liquor. These were placed in a separate bottle, for the reason given above.

Properties.—The salt so prepared gave dark red crystals which were octahedral in form, very soluble in warm water, but insoluble in organic solvents. Dilute nitric or hydrochloric acid was without action. Strong hydrochloric produced a yellow precipitate with the evolution of chlorine. Strong nitric acid gave a precipitate, soluble on addition of water. Mercurous nitrate gave an orange-colored precipitate, insoluble on boiling, but rendered soluble by addition of a few drops of nitric acid. Barium chloride produced no change in the cold, but on warming, a light yellow precipitate came down.

Method of Analysis.—The salt was treated as in former cases, except that the magnesium pyrophosphate and magnesium pyroarsenate, after weighing, were dissolved in hydrochloric acid and hydrogen sulphide passed through the solution to throw out the arsenic. Thus phosphorus pentoxide was determined by throwing out the magnesium pyrophosphate again, giving the arsenic and phosphorus either direct or by difference.

Result of Analysis :—

	Theory.	Found.	Found.	Found.	Found.
$(NH_4))_2O$	5.82	5.81	5.79	5.79	5.84
P_2O_5	2.32	2.24	2.26	2.22	......
As_2O_5	.98	.98	1.00	.81	......
V_2O_5	12.95	13.07	13.05	13.09	......
WO_3	63.98	63.85	63.86	63.67	63.91
H_2O	13.95	13.87	13.88	13.85	......
	100.00	99.82	99.84	99.35	

Ammonium Phospho Arseno-Vanadico-Tungstate.

$88(NH_4)_2O.12P_2O_5.2As_2O_5.69V_2O_3.148WO_3+484H_2O.$

Preparation.—Having made the combination of phosphorus pentoxide, arsenic pentoxide, and vanadium pentoxide, the next step was to introduce the vanadium as the trioxide. For this purpose 1 grm. of ammonium phosphate, 1 grm. of ammonium arsenate, 2 grms. of vanadium trioxide, 16 grms. of ammonium tungstate, 30c.c. of ammonium hydrate and 700c.c. of water were boiled for four hours. The greenish black solution was filtered while hot. It was then evaporated to about one-half of its original volume, and on standing over night, in a cool place, the salt was deposited. The second crop of crystals was contaminated with impurities, and could not be used for analysis.

Properties.—Greenish black octahedral crystals were produced, soluble in water, insoluble in alcohol or ether. Dilute nitric or hydrochloric acid was without action.

Strong hydrochloric acid gave a red solution, with only a slight cloudiness being formed; on addition of water a heavy yellow precipitate came down. The precipitate produced by nitric acid dissolved on the addition of water. Mercurous nitrate and barium chloride produced yellow precipitates, which remained insoluble on boiling, but dissolved when a little nitric acid was added.

Method of Analysis.—Same as in the former case, the vanadium pentoxide found being calculated to vanadium trioxide.

Result of Analysis:—

	Theory.	Found.	Found.	Found.
$(NH_4)_2O$	7.59	7.58	7.52	7.58
P_2O_5	2.82	2.88	2.81	2.84
As_2O_5	.76	.76	.73	.66
V_2O_3	17.16	17.09	17.11	17.17
WO_3	57.20	57.11	57.15	56.89
H_2O	14.47	14.38	14.36	14.24
	100.00	99.80	99.68	99.38

AMMONIUM PHOSPHO-ARSENO-VANADO-VANADICO-TUNGSTATE.

$98(NH_4)_2O.14P_2O_5.2As_2O_5.34V_2O_5.41V_2O_3.194WO_3.590H_2O.$

Preparation.—From the previous salts produced, it seemed possible to introduce vanadium in two conditions together with the phosphorus and arsenic.

To accomplish this 1 grm. of ammonium phosphate, 1 grm. of ammonium arsenate, 1 grm. of ammonium vanadate, 1 grm. of vanadium trioxide, 16 grms. of ammonium tungstate, 20 c.c. of ammonium hydrate, and 700 c.c. of water were boiled together for six hours. The filtered solution was evaporated, and allowed to stand over night to crystallize.

Properties.—The yield of salt was small. Black octahedral crystals, however, separated. On evaporation of the mother liquor the crystals, which were minute, were mixed with a large amount of other salts, from which it was difficult to separate them.

The deposit of ammonium chloride, as well as other impurities, were removed to some extent by washing with cold water, in which the crystals themselves were not very soluble. Strong hydrochloric acid decomposed the salt, liberating chlorine and giving a deposit of the hydrated oxide. Strong nitric acid gave a precipitate, soluble on addition of water. Many of the heavy metals produced precipitates that remained insoluble on boiling, but dissolved on addition of a few drops of nitric acid.

Method of Analysis.—The same method was applied as in former cases.

Result of Analysis :—

	Theory.	Found.	Found.	Found.
$(NH_4)_2O$	6.73	6.74	6.74	6.70
P_2O_5	2.62	2.54	2.37	2.41
As_2O_5	.60	.61	.62	.65
V_2O_5	8.17	8.09	8.09	8.16
V_2O_3	8.12	8.16	7.96	8.08
WO_3	59.70	59.79	59.81	59.79
H_2O	14.06	14.09	13.88	13.99
	100.00	100.02	99.47	99.78

There now remained only two more possibilities in these combinations.

Ammonium Phospho-Arsenico-Vanadico-Tungstate, and
Ammonium Phosphorico-Arsenico-Vanadico-Tungstate.

They were prepared, but the crystals obtained were not well defined, being also mixed with many impurities. After several attempts to get them, the work was given up. It seems very probable, however, that they can be obtained pure, and will be a subject for further study,

Conclusion.

The formulas as given above cannot be looked upon as being definite. The writer is well aware that other views and interpretations may be given to his results, but as even these cannot be absolutely demonstrated, he regards the written formulas as wholly tentative. They will receive further study. They may be multiples of the same, or perhaps not so complicated as would appear. As there is no method, at present, to determine the molecular magnitude of such bodies, the only recourse was the result of analysis. It will be readily seen, that a slight error in the percentage of arsenic or phosphorus would alter the whole formula. It can only be claimed that such compounds exist, and that the constitution assigned to them remains open to correction.

Acknowledgement.

I take great pleasure in expressing my appreciation of the kindness shown to me, and the interest taken in this work by Professor Edgar F. Smith, at whose suggestion the investigation was undertaken, and whose ready council, as a friend and teacher, will be a lasting inspiration.

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